

55

A13

TLC 37.481

KFKI-71-30



A. Jánossy  
G. Grüner

SATELLITE STRUCTURE  
DUE TO CHARGE PERTURBATION AROUND  
A NEARLY MAGNETIC IMPURITY

*Hungarian Academy of Sciences*

CENTRAL  
RESEARCH  
INSTITUTE FOR  
PHYSICS

BUDAPEST



KFKI-71-30

SATELLITE STRUCTURE DUE TO CHARGE PERTURBATION AROUND  
A NEARLY MAGNETIC IMPURITY

A. Jánossy and G. Grüner

Central Research Institute for Physics, Budapest, Hungary  
Solid State Physics Department

Submitted to Solid State Communications



Virtual bound states of transitional metal impurities in nonmagnetic metal matrices give rise to two well observable effects due to the redistribution of the conduction electrons: these are a spin and a charge density perturbation around the impurities. The charge density perturbation, which will be investigated in this paper, has the asymptotic form [1].

$$\Delta\rho(r) = \alpha \cos(2k_F r + \phi)/r^3 \quad /1/$$

where  $\alpha$  and  $\phi$  are the amplitude and phase of the oscillation, respectively, depending on the features of the virtual bound state [2]. Measurement of charge perturbation by NMR [2,3,4] has proved to be a very effective tool in gaining insight into the mechanism of this screening.

In a recent publication [5] it was demonstrated that the amplitude of the charge screening, which in Al - transitional metal alloys is proportional to the first order wipe-out number, is consistent with the Friedel-Anderson picture provided the impurities are assumed to be nonmagnetic and, when in Al-Mn and Al-Cr alloys the effects of localized spin fluctuations /l.s.f./ [6] are taken into consideration at finite temperatures. Increasing the temperature the decrease of the oscillation amplitude caused by the l.s.f. could be fitted well [5] to a theoretically derived formula valid for not too high values of  $T/\tilde{\theta}$ :

$$\alpha = \alpha_0 \left[ 1 - (T/\tilde{\theta})^2 \right]$$

where  $\tilde{\theta}$  a characteristic temperature depending on the lifetime of the l.s.f. is equal to 740°K and 960°K for the Al-Mn and Al-Cr systems respectively.

In the following further evidence of the presence of l.s.f. effects in a nearly magnetic aluminium alloy is provided by measurements of the temperature dependence of the charge density perturbation at sites of one of the coordinations shells of the impurities.

The charge density perturbation around impurity atoms gives rise to an electric field gradient /EFG/  $q(r)$ , which interacts with the quadrupole moment of the nuclei and has the form [1]

$$q(r) = \frac{8\pi}{3} \mu \Delta\rho(r)$$



where  $\mu$  is an EFG enhancement factor. The interaction may be measured by investigating the pure quadrupole resonance pattern, using field cycling techniques [7] or by measuring its effect on the nuclear Zeeman levels by continuous wave /cw/ NMR techniques. In the latter case the perturbation of the Zeeman levels and the corresponding shift of the resonance frequency in a polycrystalline sample is strongly dependent on the angle between the EFG tensor and the external magnetic field, and thus the spectrum of coordination shells not too far from the impurity are strongly broadened. On the one hand this broadening causes a decrease of the total peak-to-peak amplitude of the dilute alloy spectrum with respect to that of a pure metal sample. The slope of this decrease, the first order wipe-out number, is proportional to the amplitude and is insensitive to the phase of the oscillation [8]. This method was applied in [5] to determine the oscillation amplitude. On the other hand, the spectra due to nuclei belonging to a single shell have a characteristic structure, which under optimal circumstances may be detected as satellite lines.

This latter effect was investigated in the Al-Cr dilute alloy system. Thin-foil sandwich-type samples having Cr concentrations of 0.2 and 0.4 at% were used. The details of sample preparation, heat treatment and analysis are described in [4]. Corrections due to eddy current distortion were found to be negligible. The measurements at 4.2°K were performed on a conventional cw NMR spectrometer [9] in the frequency range 3-8.5 MHz. Measurements at temperatures other than 4.2°K were performed at 7 MHz; in this case averaging of several spectra on a small computer /type TPA/ was used to obtain a five-fold increase in the signal-to-noise ratio over that of a single run with a time constant of 100 sec.

The spectra of the two alloys are very similar, the main feature being the occurrence of two pairs of weak satellite lines beside the strong main line /Fig. 1/. As measured at 4.2°K at several points between 3 and 8.5 MHz /Fig. 2/ the positions of the satellite peaks relative to the centre of the main line were frequency independent within 2%, although the high-field side of the spectrum exhibited an additional field-dependent component at about 25 G from the center as shown in Fig. 1. The frequency independence and symmetry of the satellite line pattern gives evidence of a pure first order quadrupole splitting with no observable spin density perturbation at the observed sites. The satellite peaks can be attributed to the singularities in the polycrystalline spectra of the  $5/2 \rightarrow 3/2$  and  $3/2 \rightarrow 1/2$  transitions of  $\text{Al}^{27}$  nuclei feeling a perturbation with a quadrupole coupling constant  $\nu_Q = e^2 q Q / 2I(2I-1)h$  [10].  $q$  is the main component of the EFG tensor at a certain shell around the impurities due to the charge density perturbation. The peaks of the satellite lines are at roughly  $\pm 1/2 \nu_Q$



and  $\pm \nu_Q$ , assuming an axially symmetric EFG [11]. The quadrupole coupling constant was found to be  $66 \pm 1$  kHz at  $4.2^\circ\text{K}$ , taking into account a small correction of 2 kHz due to dipole-dipole and inhomogeneous quadrupole broadening. The pure quadrupole resonance spectra reported by Minier and Bertier [12] contains - among others - strong peaks at 70 and 135 kHz in fair agreement with our value of  $\nu_Q$  supporting these peaks to be due to the  $3/2 \rightarrow 1/2$  and  $5/2 \rightarrow 3/2$  transitions respectively. The amplitude ratio of the outer satellites to the central resonance is  $2 \pm 0.5\%$ . Although the estimate of the corresponding number of sites is hampered by uncertainties in the shape of the  $5/2 \rightarrow 3/2$  component of the main line, it could be concluded that it arises from the seventh or a further coordination shell of the impurities containing a large number of sites. From this we believe that the asymmetry parameter is negligible, and so further corrections of  $\nu_Q$  are unnecessary.

Fig. 3 shows the variation of the positions of the two outer peaks with temperature. It should be contrasted with the findings of Drain [13], who did not observe any temperature dependence on studying similar satellite lines in dilute Al-Zn alloys. This gives further support to our view that the temperature dependence is particular to nearly magnetic impurities in aluminium. As it can be seen from Fig. 3., a rather good agreement is found with an expression  $1 - (T/\vartheta)^2$  using  $\vartheta = \pm 860 \pm 100^\circ\text{K}$ . This value is equal within experimental errors to the characteristic temperature determined by the oscillation amplitude measurements of [5]. As  $\nu_Q$  reflects the charge perturbation at a certain distance from the impurities, it is sensitive to both the amplitude and phase of the charge oscillation, whereas the first order wipe out number is proportional to the amplitude only. The above equality suggests that no drastic change occurs in the phase of the charge density oscillation. Theoretical considerations by Hargitali [14] have proved this to be the case for nearly magnetic impurities having a virtual bound state just at the Fermi level.

Finally we would like to mention, that experiments measuring the local properties at near neighbours of the impurities are not influenced by impurity-impurity interactions. Further advantage of the present measurements is that no corrections of the type occurring for example in resistivity measurements due to the temperature dependence of the pure matrix are necessary.



#### ACKNOWLEDGEMENTS

We are grateful to Prof. L. Pál and Dr. K. Tompa for their continuous interest in this work, to dr. C. Hargitai and A. Zawadowski for helpful discussions. We would also like to thank Dr. M. Minier for communicating results in advance of publication and Drs. E. Csetényi and R. Vassel for supplying samples.

#### REFERENCES

- [1] W. Kohn and S.H. Vosko; Phys. Rev., 119, 912 /1960/
- [2] J.M. Brettel and A.J. Heeger; Phys. Rev., 153, 319 /1967/
- [3] K. Tompa; J. Phys. Chem. Sol., /to be published/
- [4] G. Grüner, E. Kovács-Csetényi, K. Tompa and C.R. Vassel; Phys. Stat. Sol. /to be published/
- [5] G. Grüner and C. Hargitai; Phys. Rev. Letters, 26, 772 /1971/
- [6] P. Lederer and D.L. Mills; Phys. Rev., 165, 387 /1967/  
N. Rivier and M.J. Zuckermann; Phys. Rev. Letters, 21, 904 /1968/  
C. Hargitai and G. Corradi; Solid State Comm., 7, 1535 /1969/
- [7] M. Minier; Phys. Rev., 182, 437 /1969/
- [8] K. Tompa, G. Grüner, A. Jánossy and F. Tóth; Solid State Comm., 7, 697 /1969/
- [9] K. Tompa, F. Tóth; Magyar Fizikai Folyóirat, 11, 177 /1963/
- [10] M.N. Cohen and F. Reif; in "Solid State Physics" ed: F. Seitz and D. Turnbull, Academic Press N.Y. Vol. 5 p. 321
- [11] L. E. Drain; Proc. Phys. Soc., 88, 111 /1966/
- [12] M. Minier and G. Bertier private communication
- [13] L.E. Drain; J. Phys. Chem. Ser., 2 1, 1690 /1968/
- [14] C. Hargitai; private communication



# FIGURE CAPTIONS

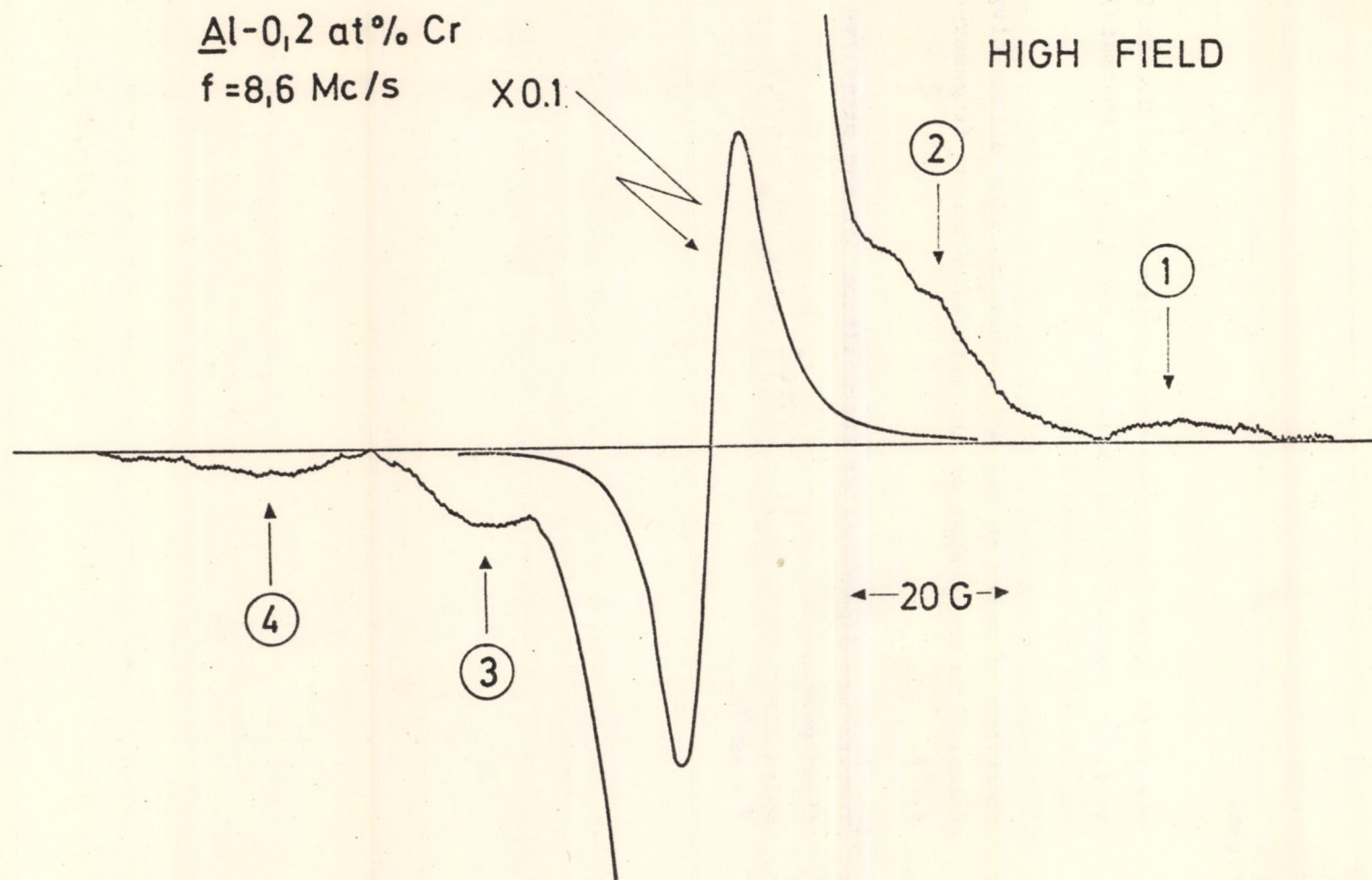
Fig. 1 : Satellite structure of the NMR spectrum of Al + 0.2 at% Cr at 4.2°K. Amplification during the recording of the main line was reduced by a factor of 10.

Fig. 2 : Positions of peaks in the NMR spectra of AlCr dilute alloys relative to the center of the main line versus frequency at 4.2°K.

Fig. 3 : Temperature dependence of the position of the outer low field peak .

Solid line  $\Delta H = \Delta H_0 \left[ 1 - \left( T/\bar{\theta} \right)^2 \right]$  with  $\Delta H_0 = 60$  G,  
 $\bar{\theta} = 860^\circ\text{K}.$







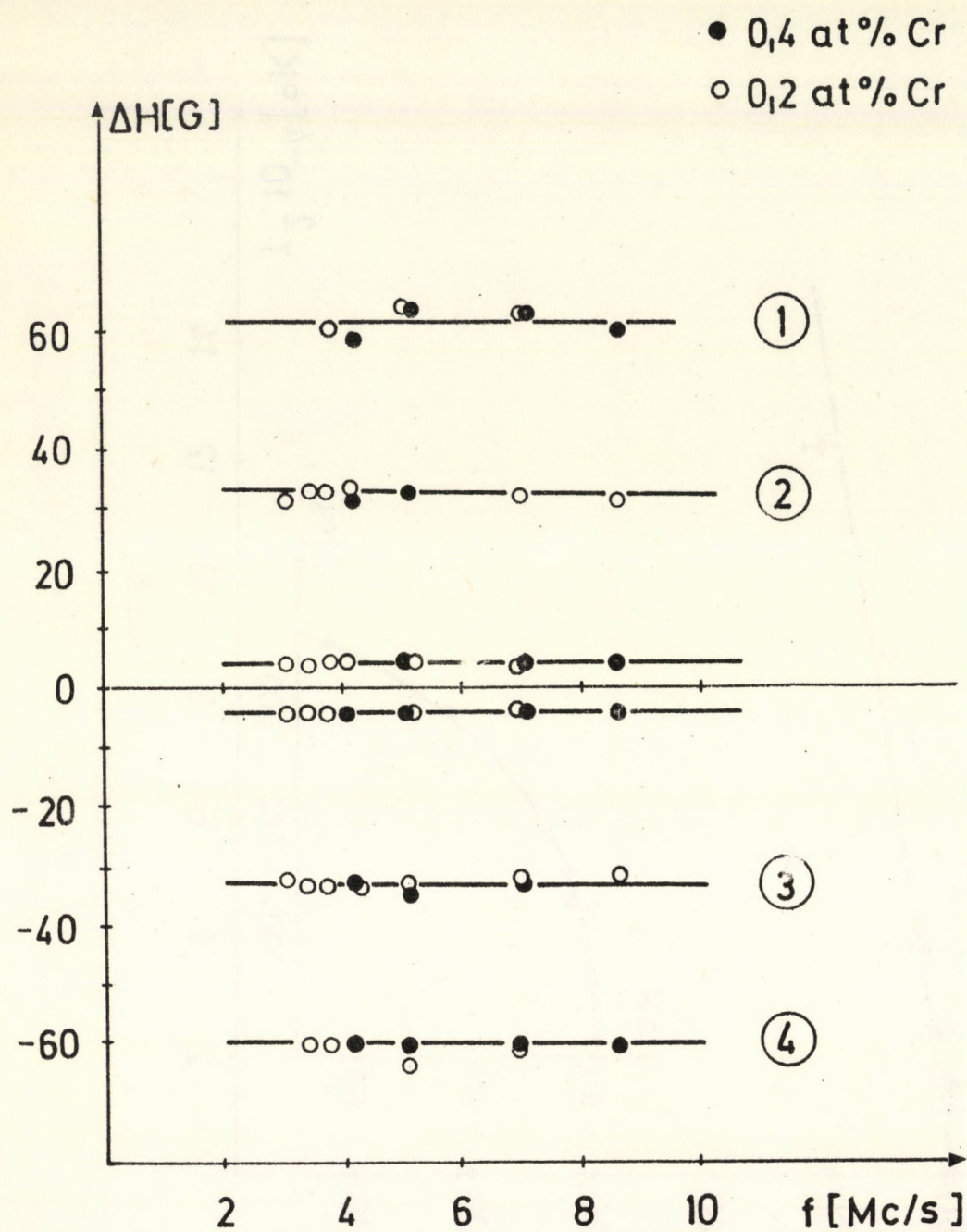


Fig. 2



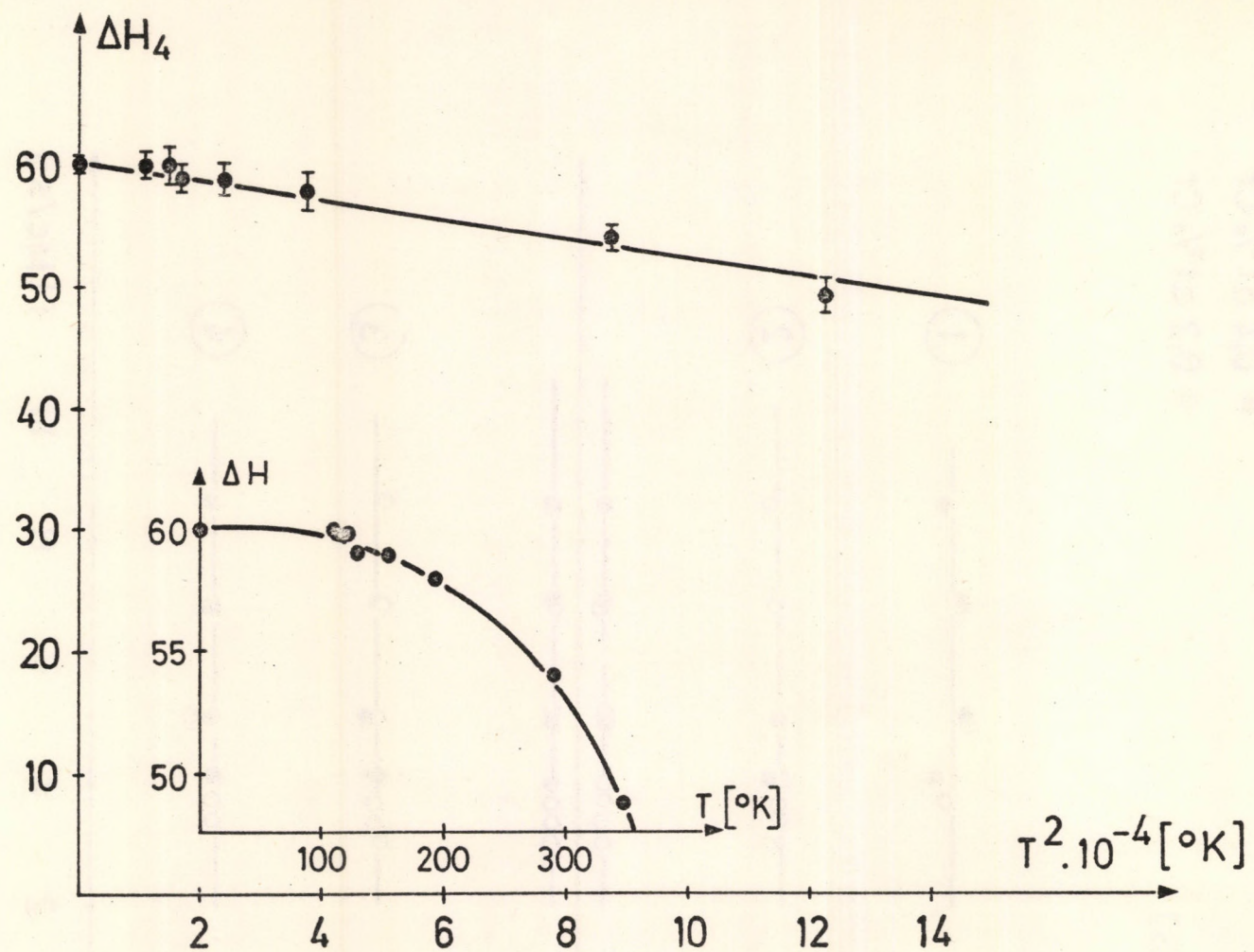


Fig. 3







### ABSTRACT

The satellite structure of  $Al^{27}$  NMR spectra in dilute Al-Cr alloys due to first order quadrupole splitting on a certain coordination shell of the impurities was investigated. The temperature dependence of the electric field gradient at this shell is compared with recent NMR measurements of the charge density oscillation amplitude and further support is adduced for the theory of localized spin fluctuations in alloys containing nearly magnetic impurities.

### РЕЗЮМЕ

Обнаружено квадрупольное расщепление ЯМР спектра  $^{27}Al$  в сплаве Al-Cr. Градиент электрического поля возникает вследствие присутствия примесных атомов, а величина расщепления зависит от расстояния ядра  $^{27}Al$  от примесного атома. Амплитуда осцилляции зарядовой плотности, измеренная ранее с помощью ЯМР, сопоставляется с температурной зависимостью квадрупольного расщепления. Результаты измерения подтверждают теорию флуктуации локализованных спинов.

### KIVONAT

Az Al-Cr rendszer  $^{27}Al$  magok MMR spektrumában szatellit szerkezetet figyeltünk meg, amely a szennyezések körüli valamely koordinációs héjon fellépő elsőrendű kvadrupól felhasadásból származik. Az ezen a héjon fellépő elektromos térgradiens hőmérséklet függését összehasonlítottuk a töltéssűrűség oszcilláció amplitudójának korábbi MMR mérésével. A mérések a lokalizált spinfluktuációk elméletének újabb alátámasztását adják.

















Kiadja Központi Fizikai Kutató Intézet  
Felelős kiadó: Pál Lénárd igazgató  
Felelős szerkesztő: Dr. Tompa Kálmán  
a KFKI Szilárdtestfizikai Tudományos  
Tanácsának elnöke  
Szakmai lektor: Hargitai Csaba  
Nyelvi lektor: T. Wilkinson  
Példányszám: 330 Törzsszám: 71-5663  
Készült a KFKI sokszorosító üzemében,  
Budapest  
1971. május hó